PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01J 2/28, C04B 18/02 — A1

(11) International Publication Number: **WO 97/33685**

(43) International Publication Date: 18 September 1997 (18.09.97)

(21) International Application Number: PCT/NL97/00059

(22) International Filing Date: 13 February 1997 (13.02.97)

(30) Priority Data:
1002344 14 February 1996 (14.02.96) NL

(71) Applicant *(for all designated States except US)*: DSM N.V. [NL/NL]; Het Overloon 1, NL-6411 TE Heerlen (NL).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: COURAGE, Antonius, Johannes, Franciscus, Maria [NL/NL]; Belikstraat 12, NL-6129 PP Stein (NL). FRIEDERICHS, Joseph, Petronella [NL/NL]; Wilhelminalaan 23, NL-6017 BA Thorn (NL).

(74) Agent: DORRESTIJN, Antoon; Octrooibureau DSM, P.O. Box 9, NL-6160 MA Geleen (NL).

(81) Designated States: AL, AU, BA, BB, BG, BR, CA, CN, CU, CZ, EE, GE, HU, IL, IS, JP, KP, KR, LC, LK, LR, LT, LV, MG, MK, MN, MX, NO, NZ, PL, RO, SG, SI, SK, TR, TT, UA, US, UZ, VN, YU, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
In English translation (filed in Dutch).

(54) Title: METHOD FOR PREPARING A MORTAR

(57) Abstract

Method for preparing a concrete mortar which contains a fraction of inorganic grains having a diameter < 500 μm, wherein the fraction containing the inorganic grains is added in the form of a granular material which contains the inorganic grains which, with the aid of a water-soluble polymer, are bound so as to form the granular material. As a result, a homogeneous mortar is obtained.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic	SD	Sudan
CF	Central African Republic		of Korea	SE	Sweden
CG	Congo	KR	Republic of Korea	SG	Singapore
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LR	Liberia	SZ	Swaziland
CS	Czechoslovakia	LT	Lithuania	TD	Chad
CZ	Czech Republic	LU	Luxembourg	TG	Togo
DE	Germany	LV	Latvia	TJ	Tajikistan
DK	Denmark	MC	Monaco	TT	Trinidad and Tobago
EE	Estonia	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	UG	Uganda
FI	Finland	ML	Mali	US	United States of America
FR	France	MN	Mongolia	UZ	Uzbekistan
GA	Gabon	MR	Mauritania	VN	Viet Nam

METHOD FOR PREPARING A MORTAR

The invention relates to a method for preparing a mortar which contains a fraction of inorganic grains having a diameter <500 μm.

The term mortar refers to a mixture which contains a binder, a filler, preferably sand, and water.

There is a need for admixing mortar, for example concrete mortar, with a fraction of inorganic grains having a diameter <500 μm, hereinafter referred to as fine fraction. As a result the total filler content of the product which is prepared from the mortar, such as, for example, concrete or sand-lime brick can increase, and the mechanical properties of the product are improved. This also makes it possible for a smaller amount of binder such as, for example, cement, to be added to the mortar, while the product which is formed from the mortar still has adequately good mechanical properties.

A problem in the preparation of such a mortar is that the fine fraction, which is generally added separately from the other fillers, mixes only very slowly and often incompletely with other components of the mortar. Consequently the advantages which could be achieved by the addition of the fine fraction are not or only partially achieved. Thus it is then again often necessary to add an excess of binder to the mortar, the drawbacks being that the product prepared from the mortar is less durable, suffers from increased shrinkage and has a higher cost price.

Solutions to the above-mentioned problem have been sought in the past, without a solution having been found with which the desired result was achieved.

It is an object of the present invention to provide a method for preparing a mortar which does not have the abovementioned drawbacks.

This object is achieved, surprisingly, by the fine fraction, in the method according to the invention, being added in the form of a granular material which contains the inorganic grains fraction, which grains, with the aid of a water-soluble polymer, are bound so as to form the granular material.

This ensures that the fine fraction is mixed rapidly and well, so that a homogeneous mortar is obtained.

A further advantage is that the granular material can be readily handled, whereas the fine fraction as such, for example fine sand, is virtually impossible to handle. When transferred, the fine sand will dust and thus presents a health hazard. Moreover, the fine sand is very cohesive and therefore agglomerates and causes bridging in the hopper of a storage vessel, whereupon the sand is unable to flow through the hopper. The granular material in contrast can be readily handled, does not dust and easily flows through a hopper. Furthermore, the mortar which contains the fine fraction of the inorganic grains can be prepared in a simple manner with the aid of the methods and equipment known therefor, because the water-soluble polymer which binds the grains so as to form the granular material dissolves in the water of the mortar.

Examples of suitable material of which the inorganic grains may consist are silicon oxide-containing and calcium carbonate-containing materials such as, for example, fly ash, quartz, blast furnace slags, limestone and sand. Preference is given to the use of sand or limestone.

Examples of water-soluble polymers which can

be used are poly(vinyl alcohol), poly(acrylic acid), poly(methacrylic acid), poly(vinyl acetate), copolymers containing monomer units of vinyl alcohol, acrylic acid, maleic anhydride and vinyl acetate cellulose, and also salts of the above-mentioned polymers and copolymers.

Preferably, the grains of the fine fraction have a diameter <250 μm, more preferably <130 μm.

As a result the granular material is, for example, very suitable for use in the preparation of concrete which has a high compression strength and low water penetration.

A granular material employed in the method according to the invention preferably disintegrates very rapidly in water. Were the granular material to retain its consistency over a very long period during the preparation process of the concrete mortar, after the granular material has been added and been blended into the mixture of water and other components, this would unnecessarily delay the preparation process. Preferably, the granular material disintegrates within 600 seconds in water of 23°C, more preferably within 300 seconds, even more preferably within 60 seconds.

Even more preferably, a granular material used in the method according to the invention disintegrates so quickly in water that the granular material is first mixed completely and homogeneously through the mortar, before the granular material disintegrates. As a result, a highly homogeneous mortar is obtained which contains no agglomerates of the fine fraction or only very few of them. Additionally, this provides a very rapid mixing process.

The speed with which the granular material disintegrates can be influenced, for example, by the choice of the water-soluble polymer, the diameter of the granular material and the amount of water-soluble

polymer contained in the granular material, based on the fine fraction of inorganic grains.

Very good results are obtained if the granular material has still not disintegrated after 2 seconds, more preferably after 5 seconds, even more preferably after 10 seconds in water of 23°C. The time after which the granular material has disintegrated in water is determined by 95 grams of water at 23°C in a glass beaker having a volume of 250 ml and a diameter of 66 mm being stirred with a cylindrical magnetic stirrer having a diameter of 8 mm and a length of 40 mm, the stirrer speed being 625 revolutions per minute, 5 grams of the granular material being added to the water and the time then being determined at which the granular material has completely disintegrated.

Preference is given to the use, in the method according to the invention, of a granular material which has a strength of at least 30 N, preferably at least 40 N, even more preferably at least 50 N. Since such a granular material readily withstands forces which, for example, are exerted on the granular material during storage, transportation and during the addition, it is ensured that the granular material in the process retains its consistency well and does not suffer from crumbling or attrition, which again may give rise to the problems which manifest themselves during the use of a fine fraction which is not in the form of the granular material.

The strength of the granular material is determined by a granule being positioned between two parallel planar plates, the plates being moved towards one another in the direction perpendicular to the plates until the granule yields, the force being measured which has to be exerted on the plates, this being carried out for 10 grains from the granular material composition, and the average of the 10

measured forces being calculated.

Preference is given to the use, in the method according to the invention, of a granular material in which the water-soluble polymer used is the salt of a polymer which contains monomer units of styrene and of maleic anhydride (SMA polymer). Such a granular material has a beneficial dissolution rate and good strength. Preference is given to the use of the sodium salt or potassium salt of the SMA polymer. The salt of the SMA polymer can be prepared in a simple manner by the polymer, preferably as a powder, being combined, for example at a temperature of 20-150°C and a pressure of 1-10 bar, with a solution of sodium hydroxide or potassium hydroxide and the mixture thus obtained then being stirred until the polymer in the form of the salt has dissolved.

The SMA polymer can be prepared with the aid of one of the known methods as described, for example, in Hanson and Zimmerman, Ind. Eng. Chem. Vol. 49, No. 11 (1957), pp. 1803-1807.
The SMA polymer contains, for example, 10 - 50 mol% of maleic anhydride monomer units. Preferably the SMA copolymer contains 15 - 50 mol%, even more preferably 20 - 45 mol% of maleic anhydride monomer units. In addition to monomer units of styrene and maleic anhydride, the SMA polymer may contain monomer units of, for example, acrylic acid, methacrylic acid, an ester of these acids, acrylonitrile, α-methylstyrene, etc. By virtue of the presence of the acrylic acids, particularly if the maleic anhydride monomer units content is relatively low, the water-solubility of SMA polymer and the salt of the SMA polymer is improved yet further.

The intrinsic viscosity of the SMA polymer is, for example, 0.2 - 0.8 dl/g. Preferably, the intrinsic viscosity is 0.3 - 0.6 dl/g, because a

solution can be made therefrom which is very suitable for use in the preparation of the granular material. Thus a solution having a relatively high concentration of the SMA polymer can be prepared which still has a sufficiently low viscosity.
Preferably, the SMA polymer comprises 20 - 50 mol% of maleic anhydride monomer units and 80 - 50 mol% of styrene monomer units, and the intrinsic viscosity is 0.3 - 0.6 dl/g.
The granular material can be prepared by the inorganic grains being mixed with a solution of the water-soluble polymer in water, for example in a mixing ratio of 1 - 4.5 parts by weight of water-soluble polymer, 10 - 30 parts by weight of water and 100 parts by weight of inorganic grains, the mixture thus obtained then being dried, for example by the mixture being heated to a temperature of 60 - 90°C in an oven, and the dry mixture being ground to produce the granular material. Preferably, the mixture is dried in a rotary oven or on a granulating disc, the granular material being formed directly during drying.

Preferably, the granular material is prepared by coarse sand being ground to fine sand which is then employed for implementing the above-mentioned method. This has the advantages that, after grinding, only a small number of operations need be carried out involving the fine sand as such, and the fine sand need not be extracted from the environment with the aid of complicated techniques. Yet another advantage is that it is thus possible to obtain a very pure fine fraction. The granular material can have various shapes and sizes. Preferably, the granular material has a weight average grain diameter of 1 - 30 mm, more preferably 2 - 10 mm. Preferably, the granules are monodisperse, so that the grains disintegrate at the same rate.

The granular material according to the invention can in general be used in any known concrete mortar.

Good results are achieved if 1 m^3 of mortar is admixed with 20 - 450 kg of the granular material.

Additionally, the mortar may contain the other components customary for mortars, such as, for example, cement or unslaked lime as a binder, coarse sand having a diameter up to 2 mm, and particles having a diameter greater than 2 mm, such as, for example, gravel, grains of limestone and of granite. The mortar may also contain aids. Aids are substances which affect the processing characteristics of the mortar and/or properties of the product prepared from the mortar. Examples of aids are accelerator, retardant, plasticizer, colorants and the like.

Examples of mortars are concrete mortar, masonry mortar, mortar for repairs, mortar for the preparation of sand-lime brick, bentonite mortar, plaster mortar, pointing mortar, lime mortar.

The composition and the preparation of concrete mortar is described, for example, in Fibre reinforced cements and concretes (1989), ISBN 1-85166-415-7 and Structurally chemically stable polymer concretes (1971), ISBN 0-7065-1137-9.

The proportioning sequence, the mixing equipment and the other conditions in the preparation of the mortar are known to those skilled in the art and depend, for example, on the type of mortar.

The mortar can be prepared, for example, by water with or without one or more of the other components of the mortar being introduced into a mixer and being mixed, the granules then being added and the mix being further mixed until the water-soluble polymer has dissolved and the fine fraction is dispersed homogeneously throughout the mix, and the other

components of the mortar then, if appropriate, being added to the mix.

It is also possible for the dry components of the mortar and the granular material to be premixed in the mixer and the water to be added afterwards. The invention also relates to the granular material which is employed in the preparation of the mortar according to the invention.

Preferably the granular material in addition to the fine fraction contains one or more of the aids. Thus it is no longer necessary for the aids to be apportioned separately.

It is possible for the granular material, in addition to the inorganic grains of the fine fraction, also to contain other inorganic grains, although this is not preferred. Thus it is possible, in the course of the preparation of the fine fraction, for example by grinding coarse sand, for a portion of the mass of grains thus produced to contain not only the fine fraction but also grains having a larger diameter, which are introduced into the granular material together with the fine fraction. Preferably, at least 70 wt.%, more preferably at least 90 wt.%, of the total mass of inorganic grains contained in the granular material consists of the fine fraction.
In a yet further improved embodiment, at least 95 wt.% of the inorganic grains contained in the granular material have a diameter <500 μm, preferably <250 μm, yet more preferably a diameter between 2 and 130 μm.

Example I

Coarse sand having a grain diameter of 0.5-3 mm was ground to fine sand having a particle diameter of 3-100 μm.

In a stirred vessel, 100 grams of a powder of SMA polymer consisting of 66 mol% of styrene monomer

units and 34 mol% of maleic anhydride monomer units and having an intrinsic viscosity of 0.57 dl/g, 0.9 litre of water and 39 grams of potassium hydroxide were stirred at a temperature of 80°C until the SMA polymer had dissolved and the salt of the SMA polymer had formed.

In a 10 litre vessel, 5 kg of the fine sand was mixed at room temperature over a period of 5 minutes with 1 l of water and 100 g of the salt of the SMA polymer. The mixture thus obtained was then dried in a hot-air oven at 80°C.

The dry mixture was then ground with the aid of a coffee grinder to produce a granular material having a grain diameter of 1-3 mm.

At 23°C, 95 grams of water in a glass beaker having a volume of 250 ml and a diameter of 66 mm were stirred with a cylindrical magnetic stirrer having a length of 40 mm and a diameter of 8 mm at a stirrer speed of 625 revolutions per minute, use being made of a stirrer supplied by Janke and Kunkel from Germany of type ES5. The water was admixed with 5 grams of the granular material. The granular material had completely disintegrated after stirring for 60 sec.

With the aid of a standard procedure, the granular material was blended in a concrete mortar (3 kg of granular material per 50 kg of concrete mortar).

The granular material could be dispersed rapidly and uniformly throughout the concrete mortar in the mixer. Then the granular material disintegrated rapidly, and a homogeneous mortar was obtained which did not contain any agglomerates of the fine sand.

The compression strength was measured by one granule at a time being placed between two parallel planar stainless-steel plates, the plates being moved towards one another in the direction perpendicular to the plates until the granule yielded, by the force

which had to be exerted on the plates being measured, this being done for 10 grains having a diameter between 5.6 and 8 mm from the mass of granular material, and the average of the 10 measured forces being calculated. The strength was 76 N.

Example II

As in Example I, except that the SMA polymer was replaced by poly(acrylic acid) having a weight average molecular weight of 130,000 kg/kmol. The time required until the granular material disintegrated in water was measured as described in Example I. The time was 120 sec. The strength of the granular material was 80 N.

Example III

As in Example I, except that the SMA polymer was replaced by PVA S40 (poly(vinyl acetate)). After grinding, a composition of 95 wt.% of granular material and 5 wt.% of loose fine sand was obtained.

The time required until the granular material disintegrated in water was measured as described in Example I. The time was 20 min. The strength was 53 N.

C L A I M S

1. Method for preparing a mortar which contains a fraction of inorganic grains having a diameter <500 μm, characterized in that the fraction containing the inorganic grains is added in the form of a granular material which contains the inorganic grains which, with the aid of a water-soluble polymer, are bound so as to form the granular material.
2. Method for preparing a mortar according to Claim 1, characterized in that the fraction of inorganic grains used is sand and/or limestone.
3. Method for preparing a mortar according to Claim 1 or 2, characterized in that the inorganic grains have a diameter <250 μm.
4. Method for preparing a mortar according to any one of Claims 1 - 3, characterized in that a granular material is used which disintegrates within 600 seconds in water of 23°C.
5. Method according to Claim 4, characterized in that a granular material is used which disintegrates within 300 seconds in water of 23°C.
6. Method for preparing a mortar according to any one of Claims 1 - 5, characterized in that a granular material is used which disintegrates after 2 seconds in water of 23°C.
7. Method for preparing a mortar according to any one of Claims 1 - 5, characterized in that a granular material is used which disintegrates after 5 seconds in water of 23°C.
8. Method for preparing a mortar according to any one of Claims 1 - 7, characterized in that a granular material is used which has a strength of at least 30 N.
9. Method for preparing a mortar according to any one

of Claims 1 - 8, characterized in that a granular material is used in which the water-soluble polymer is the salt of a polymer which contains monomer units of styrene and of maleic anhydride.

10. Method for preparing a mortar according to Claim 9, characterized in that the sodium salt or potassium salt is used.

11. Granular material as used in the method according to any one of Claims 1 - 10.

INTERNATIONAL SEARCH REPORT

Inv tional Applicaton No
PCT/NL 97/00059

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01J2/28 C04B18/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01J C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DE 40 06 068 A (HÖLTER, HEINZ) 29 August 1991 see the whole document	1
A	EP 0 587 383 A (HALLIBURTON COMPANY) 16 March 1994 see page 3, line 39 - line 50	1,6,8
A	EP 0 111 807 A (BAYER AG) 27 June 1984	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 May 1997	22 05 97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Van Belleghem, W

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter ·tional Application No
PC./NL 97/00059

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4006068 A	29-08-91	NONE	
EP 587383 A	16-03-94	CA 2105783 A	11-03-94
		NO 933221 A	11-03-94
		US 5454867 A	03-10-95
EP 111807 A	27-06-84	DE 3246493 A	20-06-84
		AU 2213083 A	21-06-84
		BR 8306873 A	24-07-84
		JP 59120235 A	11-07-84